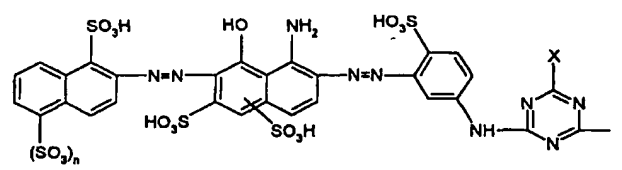
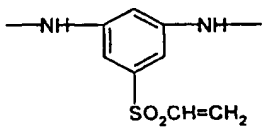


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(21) International Application Number: PCT/GB99/02447 (22) International Filing Date: 26 July 1999 (26.07.99) (30) Priority Data: 9816780.2 31 July 1998 (31.07.98) GB (71) Applicant (for all designated States except US): BASF AKTIENGESellschaft [DE/DE]; D-67056 Ludwigshafen (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): EBENEZER, Warren, James [GB/GB]; 28 Colwyn Road, Bramhall, Stockport SK7 2JQ (GB). MYNETT, Donna, Maria [GB/GB]; 44 Ashridge Avenue, Westbury Park, Newcastle-u-Lyme, Staffordshire ST6 4JA (GB). (74) Agents: COLEIRO, Raymond et al.; Mewburn Ellis, York House, 23 Kingsway, London WC2B 6HP (GB).	(81) Designated States: BR, CN, IN, JP, KR, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: REACTIVE DYES CONTAINING A LINKAGE <div style="text-align: center;">  <p>(II)</p> </div> <div style="text-align: center;"> $-Y- \text{ is } \begin{array}{c} R^1 \\ \\ -N-Z-N- \end{array} \quad (a) \quad \begin{array}{c} R^3 \\ \\ -N-Z-S- \end{array} \quad (b)$ </div> <div style="text-align: center;">  <p>(c)</p> </div> <p>(57) Abstract</p> <p>A reactive disazo dye has the formula (I) D¹-Y-D² wherein each of D¹ and D² independently is a chromophore of formula (II) in which X is fluorine, chlorine or optionally substituted pyridinium; an SO₃H is present in the 5- or 6- position of the naphthalene nucleus; n is zero or 1; and -Y- is (a); or (b) in which: Z is a C₅₋₁₂ aliphatic or aromatic cyclic hydrocarbon group, optionally additionally containing at least one hetero atom selected from N, O and S optionally substituted by at least one C₁₋₄ alkyl and SO₃H (or a salt thereof); or at least two said cyclic hydrocarbon groups linked together; or a C₁₋₁₅ alkylene or C₂₋₁₅ alkenylene chain, which chain optionally additionally contains, and/or is substituted by, other atoms or groups; and each of R¹, R² and R³, independently, is a C₁₋₄ alkyl, hydroxy-C₁₋₄ alkyl or amino-C₁₋₄ alkyl group or each of R¹ and R², together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or one of R¹, R² and R³, together with (i) the nitrogen atom to which it is attached, (ii) the substituent group on the chain Z and (iii) the chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and Y is other than (c) or a sulphonic acid salt of the dye of the formula (I).</p>		

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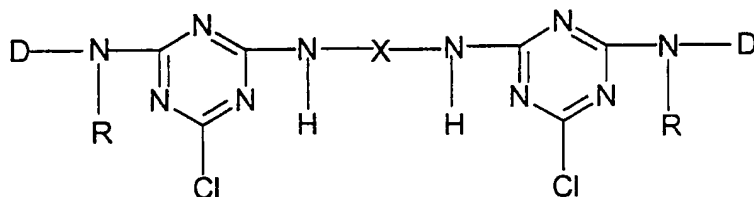
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REACTIVE DYES CONTAINING A LINKAGE

This invention relates to reactive dyes having a bridging group between triazinylamino groups each attached to a chromophore.

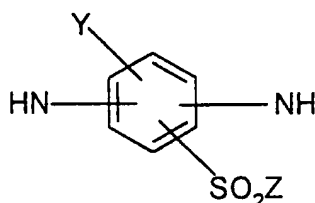
GB-A-1283771 and EP-A-0625551 disclose respective general ranges of reactive dyes of the formula (A)



(A)

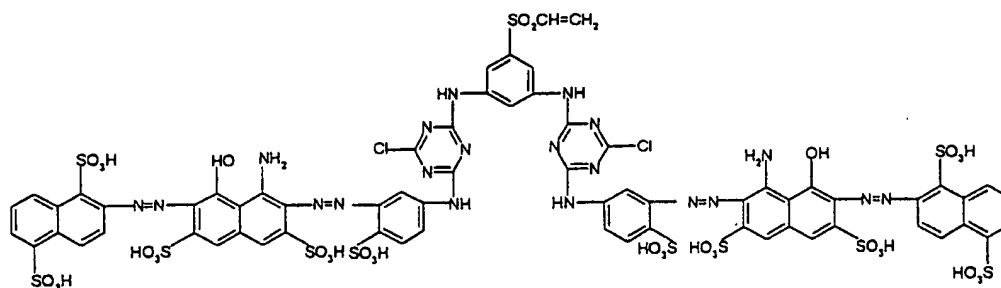
where D is a chromophore (which in the case of GB-A-1283771 is specifically a naphthylazo-phenylene or -naphthalene containing at least 3 sulphonic acid groups and in the case of EP-A-0625551 is any of a wide range of chromophores), R is H or an optionally substituted C₁₋₄ alkyl group and X specifically a linking group which, in the case of GB-A-1283771, is an aromatic group selected from phenylene, diphenylene and naphthalene nuclei, and in the case of EP-A-0625551 is an aliphatic linking group, the group -NHXNH- forming a bridging group between receptive triazine nuclei. The dyes of GB-A-1283771 offer a degree of fixation over a wide range of liquor to goods ratios and provide shades of very good light fastness, while those of EP-A-0625551 show good fastness and build up properties.

JP-A-62-172062 discloses a wide range of dyestuffs in which chromophores are linked by the specific group

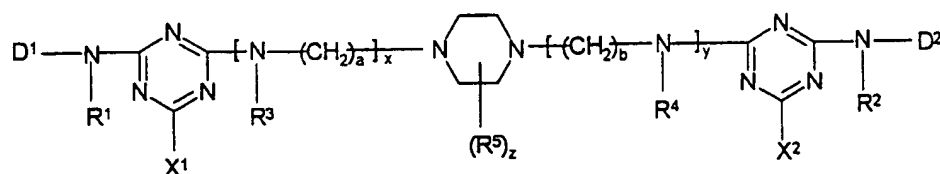


wherein Y is hydrogen, halogen or alkyl and Z is the reactive group $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$.

One of many examples of dyes disclosed has the following formula



In our WO-A-99/05224, we describe a range of dyes in which the bridging group is derived from an aminoalkyl piperazine, which dyes have the formula (B)



(B)

wherein:

each of R^1 , R^2 , R^3 and R^4 , independently, is H or an optionally substituted alkyl group;

each of X^1 and X^2 , independently, is a labile atom or group;

5 each of x and y, independently, is 0 or 1 and at least one of x and y is 1;

each of a and b, independently, is 2 to 5;

z is zero or is 1 to 4; and

when each of x and y is 1, $a > b$;

10 the or each R^5 , independently, is alkyl; and

each of D^1 and D^2 , independently, is a monoazo or polyazo chromophore, or a metallized derivative thereof.

We have found surprisingly that if, in dyes of the
15 above formula (A), the chromophore D is a particular disazo dye, defined below, then such dyes, especially when used for exhaust dyeing of cellulosic materials, can exhibit excellent all-round fastness properties and build-up and compatibility with other dyes whose preferred exhaust temperature is 80°C or, more
20 preferably, above.

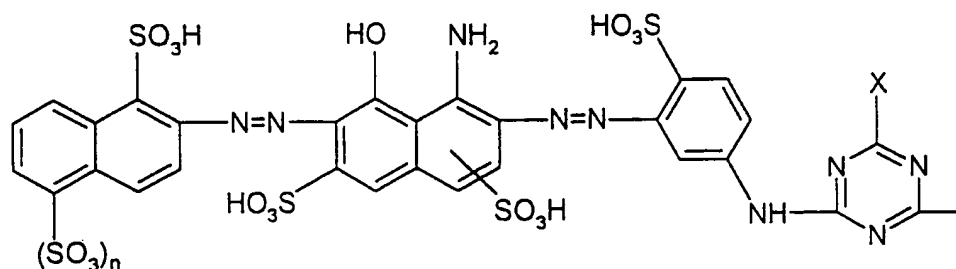
Thus, according to one aspect, the invention provides a dye of the formula (I)

25



wherein each of D^1 and D^2 independently is a chromophore of the formula

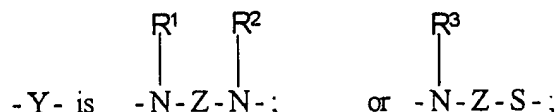
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35

in which

X is fluorine, chlorine or optionally substituted pyridinium;
an SO₃H is present in the 5- or 6- position (preferably the
6- position) of the naphthalene nucleus;
5 n is zero or 1 (preferably 1); and



10 in which

Z is a C₅₋₁₂ aliphatic or aromatic cyclic hydrocarbon group,
optionally additionally containing at least one hetero atom
selected from N, O and S and optionally substituted by at least
one of C₁₋₄ alkyl and SO₃H (or a salt thereof); or

15 at least two said cyclic hydrocarbon groups linked together;
or

a C₁₋₁₅ alkylene or C₂₋₁₅ alkenylene chain, which said chain

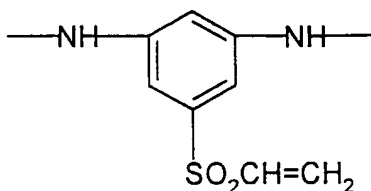
(a) optionally additionally contains, so as to be
interrupted or terminated by, at least one of (1) at least one
20 hetero atom selected from N, O and S and (2) at least one
C₅₋₁₂ aliphatic or aromatic cyclic hydrocarbon group, which said
cyclic hydrocarbon group optionally additionally contains at
least one hetero atom selected from N, O and S and is optionally
substituted by at least one of C₁₋₄ alkyl and SO₃H (or a salt
25 thereof); and

(b) is optionally substituted by C₁₋₄ alkyl, hydroxy-C₁₋₄
alkyl, amino-C₁₋₄ alkyl, hydroxyl, carboxyl or amino, which amino
group or moiety is optionally substituted by one or two C₁₋₄ alkyl
groups, or by a substituent group which, together with (i) one
30 of R¹, R² and R³ (each defined below), (ii) the nitrogen atom to
which R¹, R² or R³ is attached and (iii) a chain length of Z
between the said nitrogen and the substituent group, forms a
heterocyclic group; and

each of R¹, R² and R³, independently, is a C₁₋₄ alkyl, hydroxy-
35 C₁₋₄ alkyl or amino-C₁₋₄ alkyl group or each of R¹ and R², together

with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or (as defined above) one of R^1 , R^2 and R^3 , together with (i) the nitrogen atom to which it is attached, (ii) the said substituent group on the chain Z and (iii) the said chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and

Y is other than



(and preferably contains no reactive group); or a sulphonic acid salt of the said dye of the formula (I).

When X is a substituted pyridinium, preferred substituents are 3-carboxyl, 3-carbonamido and 4-carboxyl.

In one preferred range of dyes, Z is a C_{1-10} alkylene chain optionally substituted by at least one group selected from C_{1-4} alkyl, hydroxy and carboxyl. Such chains may be free from any hetero atom or may contain additionally at least one hetero atom selected from O and N. More preferably, the chain is a C_{2-8} -alkylene chain which is unsubstituted or substituted by at least one group selected from methyl, hydroxy and carboxyl. Still more preferably the chain is of the formula



wherein x is 2 or 3, which alkylene chain is unsubstituted or substituted by one or two methyl groups or a hydroxy or carboxyl group and each of R^1 , R^2 and R^3 independently is selected from hydrogen, C_{1-4} alkyl and hydroxyethyl.

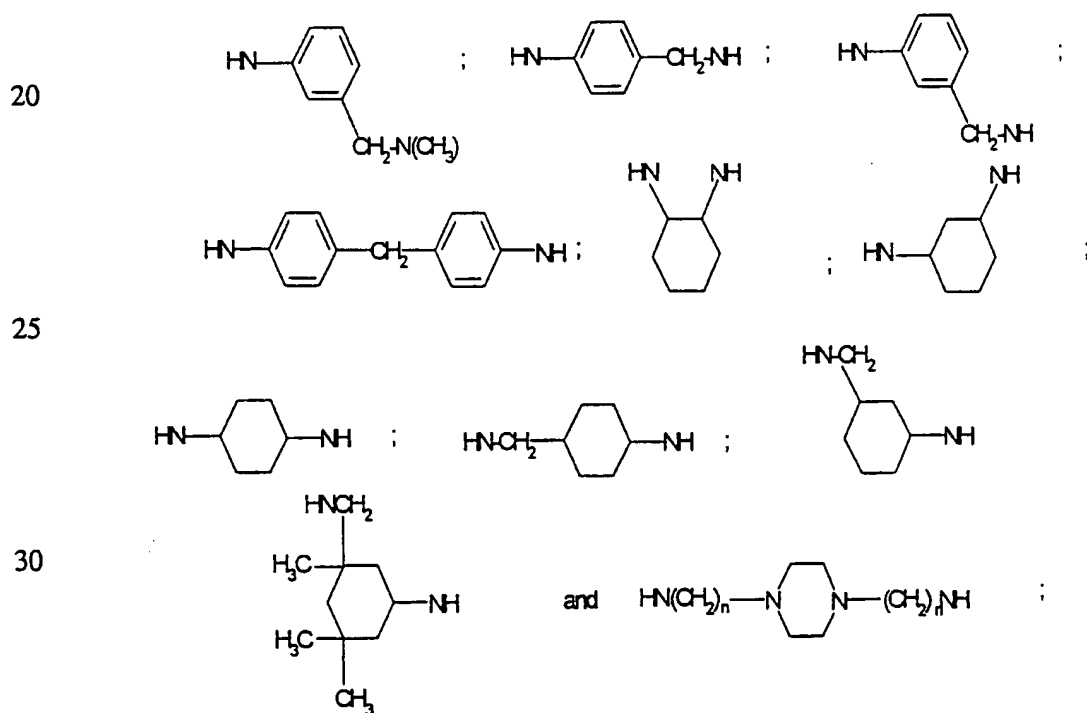
Examples of the group Y in which Z is a C₁₋₁₀ alkylene chain optionally substituted by at least one of C₁₋₄ alkyl, hydroxy and carboxyl are HNC₂H₄NH; HNC₃H₆NH; HNC₄H₈NH; HNC₅H₁₀NH; HNC₆H₁₂NH; HNC₉H₁₆NH; HNC₂H₄N(CH₃); HNC₃H₆N(CH₃); HNC₂H₄N(C₂H₄OH); HNC₂H₄N(C₃H₆OH);

5 HNC₃H₆N(C₂H₄OH); HNC₂H₄N(C₂H₅); HNC₂H₄N(n-C₃H₇); HNC₃H₆N(C₂H₅); HNC₃H₆N(n-C₃H₇); (H₃C)NC₂H₄N(CH₃); (H₃C)NC₃H₆N(CH₃); (H₃C)NC₂H₄N(C₂H₅); HNC₂H₄NH[CH(CH₃)₂]; (H₅C₂)NC₂H₄N(C₂H₅); HNC₂H₄NH[CH(CH₃)(C₂H₅)]; HNC₂H₄N(n-C₄H₉); HNC₂H₄N[CH₂CH(CH₃)(OH)]; HNCH(CH₃)CH₂NH; HNC(CH₃)₂CH₂NH; HNCH₂CH(OH)CH₂NH; HNCH₂C(CH₃)₂CH₂NH; HNCH(C₂H₅)CH₂NH;

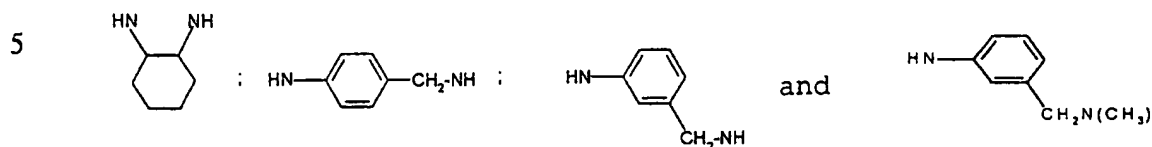
10 HNCH₂CH(CH₃)C₃H₆NH; HNCH₂CH(CH₃)N[CH(CH₃)₂]; NHCH₂C(CH₃)₂CH[CH(CH₃)₂]NH; HNC₂H₄S and HNCH(CO₂H)CH₂S.

Examples of the group Y in which Z is a C₁₋₁₀ alkylene chain additionally containing a hetero atom are HNC₃H₆N(CH₃)C₃H₆NH; HNC₂H₄OC₂H₄OC₂H₄NH; and HNC₂H₄OC₂H₄NH.

15 The C₁₋₁₀ alkylene chain of Z may additionally contain an aliphatic or aromatic ring structure and examples of the group Y in which Z is such a chain are:



where n is 2 or 3, which is an example of the group Y in which Z is C₁₋₁₀ alkylene chain interrupted by an aliphatic ring containing at least one hetero atom. Of these groups,

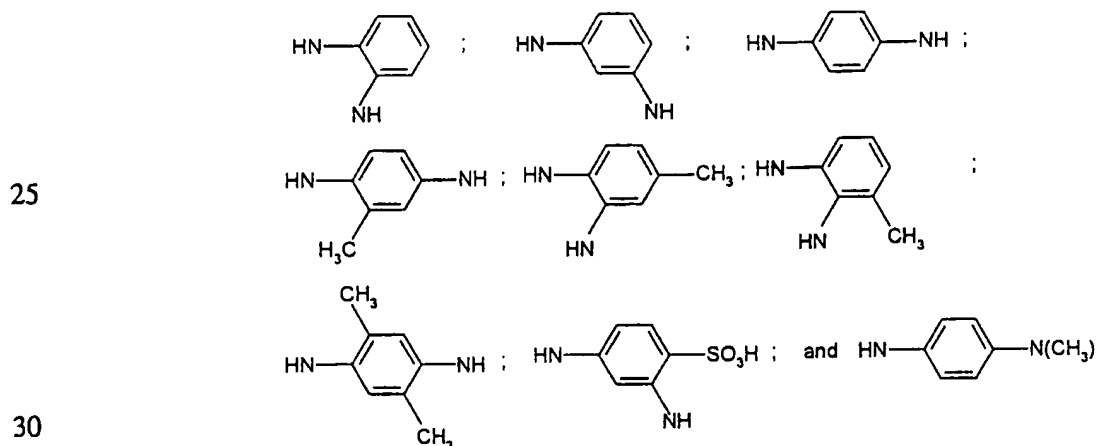


are especially preferred.

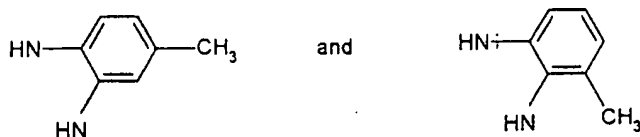
10 Especially preferred examples of the group Y in which Z is a C₁₋₁₀ alkylene chain are NHC₂H₄NH; NHC₃H₆NH; NHCH(CH₃)CH₂NH; NHC₂H₄N(CH₃); NHC₃H₆N(CH₃); NHCH₂CH(OH)CH₂NH; NHC₂H₄N(C₂H₄OH); NHC(CH₃)₂CH₂NH; NHC₃H₆N(C₂H₄OH); NHC₂H₄S; NHC₂H₄N(C₂H₅); N(CH₃)C₂H₄N(CH₃); NHC₃H₆N(C₃H₇); N(C₂H₄OH)C₂H₄N(C₂H₄OH); HNCH(CO₂H)CH₂S;
 15 N[CH(CH₃)₂]CH(CH₃)CH₂NH; HNC₆H₁₂NH; HNC₃H₆N(CH₃)C₃H₆NH; HNC₂H₄OC₂H₄NH; and HNC₂H₄OC₂H₄OC₂H₄NH.

In another preferred range of dyes, Z is a phenylene group, optionally substituted by a sulphonic acid group or one or more methyl group(s). Examples of the group Y in which Z is a phenylene group are:

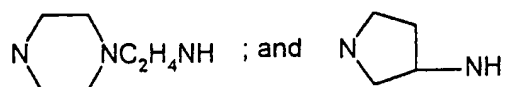
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or mixtures thereof, for example, a mixture of

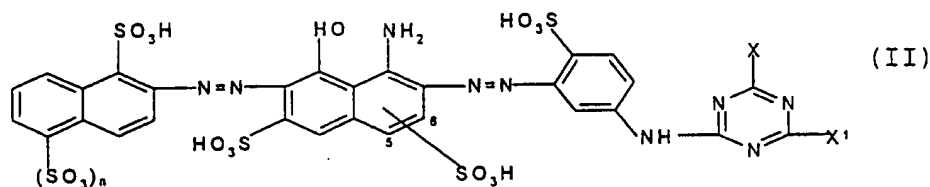


10 In yet another preferred range of dyes Z is a C_{1-15} alkylene chain and is substituted by a substituent group, preferably a C_{1-10} alkylene group, which, together with (i) one of R^1 , R^2 and R^3 , (ii) the nitrogen atom to which R^1 , R^2 or R^3 is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group. More preferably, the C_{1-15} alkylene chain is interrupted by a nitrogen atom which carries the substituent group, for example, in the case where Y is an imino- C_{1-14} alkylpiperazinyl group. Examples of Y in which the group Z includes a heterocyclic ring formed in this manner are:

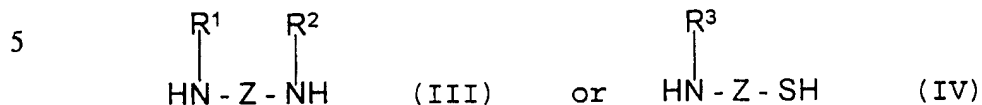


25 In another preferred range of dyes, each of R^1 and R^2 , together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, form a heterocyclic group, more preferably a piperazine group.

30 A dye of the formula (I), given and defined above, can be prepared by a method aspect of the invention, which method comprises allowing at least one reactive disazo dye of the formula (II)



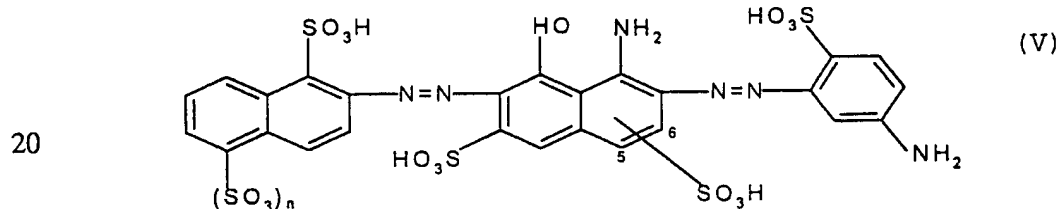
wherein X and n are as defined above and X¹ is a fluorine, chlorine or optionally substituted pyridinium group, to react with a diamine or thioamine of the formula



wherein each of R¹, R², R³ and Z is as defined above, at a pH of from 7 to 10, in a proportional amount of two moles of reactive disazo dye (II) per mole of diamine or thioamine (III) or (IV).
10 The reaction may take from 1 - 12 hours.

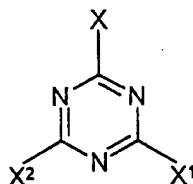
The reactive disazo dye of the above formula (II) can be prepared by reacting a disazo dye of the formula (V)

15



25 with a triazine of the formula

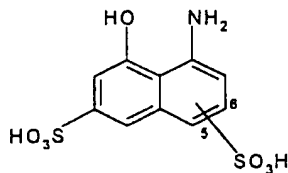
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wherein each of X, X¹ and X² independently is chlorine, fluorine or optionally substituted pyridinium.

35

The disazo dye of the formula (V) may be prepared by firstly diazotising 4-acetylamino-2-aminobenzene sulphonic acid and coupling in acid conditions (pH of 2) onto a hydroxynaphthylamine of the formula



and secondly diazotising 2-aminonaphthalene-1,5-disulphonic acid and coupling in neutral conditions (pH of 7) onto the hydroxynaphthylamine. Thereafter, removal of the acetyl protecting group of the amino group meta to the azo linkage yields the disazo dye of the formula (V).

Although dye formulae have been shown in the form of their free acid in this specification, the invention also includes dyes and processes using dyes in the salt form, particularly their salts with alkali metals such as the potassium, sodium, lithium or mixed sodium/lithium salt.

The dyes may be used for dyeing, printing or ink-jet printing, for example, of textile materials and paper.

The process for colouration is preferably performed at a pH of 7.1 to 13, more preferably 10 to 12. pH levels above 7 can be achieved by performing the process for colouration in the presence of an acid-binding agent.

The substrate may be any of a textile material, leather, paper, hair or film, but is preferably a natural or artificial textile material containing amino or hydroxyl groups, for example textile material such as wool, silk, polyamides and modified polyacrylonitrile fibres, and more preferably a cellulosic textile

material, especially cotton, viscose and regenerated cellulose, for example, that commercially available as Tencel. For this purpose the dyes can be applied to the textile materials at a pH above 7 by, for example, exhaust dyeing, padding or printing. Textile materials are coloured bright shades and possess good fastness to light and wet treatments such as washing.

The new dyes are particularly valuable for colouring cellulosic textile materials. For this purpose, the dyes are preferably applied to the cellulosic textile material at a pH above 7 in conjunction with a treatment with an acid-binding agent.

Preferred acid-binding agents include alkali metal carbonates, bicarbonates, hydroxides, metasilicates and mixtures thereof, for example, sodium bicarbonate, sodium carbonate, sodium metasilicate, sodium hydroxide and the corresponding potassium salts. The dyes benefit from excellent build-up and high fixation.

At least for cellulosic materials, dyeing may be carried out at a temperature of from 80 to 105°C, preferably 85 to 95°C, still more preferably at about 90°C, a somewhat higher temperature as compared with dyeing carried out with conventional monochlorotriazine exhaust dyes which are generally dyed at temperatures of about 80°C. By operating at this temperature, particularly improved migration is obtained.

The new dyes can be applied to textile materials containing amine groups, such as wool and polyamide textile materials, from a neutral to mildly alkaline dyebath. The dyeing process can be carried out at a constant or substantially constant pH, that is to say the pH of the dyebath remains constant or substantially constant during the dyeing process, or if desired the pH of the dyebath can be altered at any stage of the dyeing process.

The dyes may be in liquid or solid form, for example in granular or powdered form.

We find surprisingly that such dyes provide the following advantageous properties:

- 5 a) good all-round fastness;
- b) exceptionally good build-up, especially at a dyeing temperature of 90°C;
- c) very strong dyeing;
- d) exceptionally good robustness to changes in dyeing
- 10 conditions, especially temperature, pH and, in particular, dyebath liquor to substrate ratio, leading to overall excellent shade reproducibility;
- e) good wash off;
- f) good fixation;
- 15 g) good aqueous solubility; and
- h) good compatibility with other dyes of this type.

Especially preferred embodiments of the invention will now be described in more detail with reference to the following Examples

20 in which all parts and percentages are by weight unless otherwise stated. Although preparation and dyeing with any single dye is exemplified, particular advantages can be seen when dyeing with mixtures of dyes.

25 Example 1

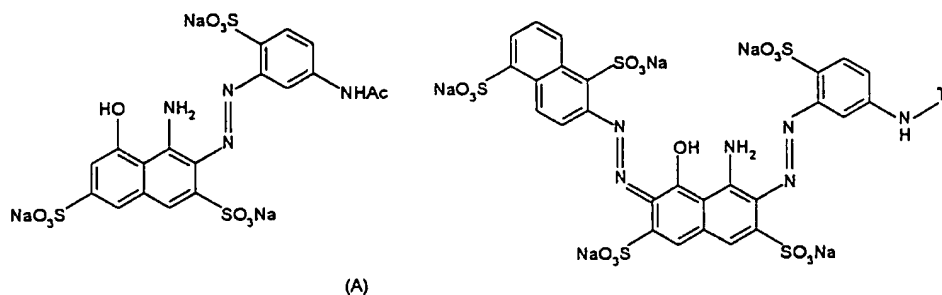
 An aqueous solution of sodium 4-acetylamino-2-aminobenzenesulphonate (0.75 mole) and sodium nitrite (390 ml 2N) was added to stirred ice (1 kg) containing concentrated hydrochloric acid (150 ml) over 30 minutes maintaining the

30 temperature below 5°C. Excess nitrite was decomposed with 10% sulphamic acid solution. An aqueous solution of the sodium salt of H-acid (0.5 mole in 600 ml) was added slowly to the well-stirred diazonium salt solution over 45 mins below 5°C at pH 2. The mixture was stirred below 5°C for 2 h, and then allowed to warm to

room temperature overnight. The intermediate (A) was screened off and dried to a damp paste at 40°C.

5

10



(B) T = acetyl

(C) T = H

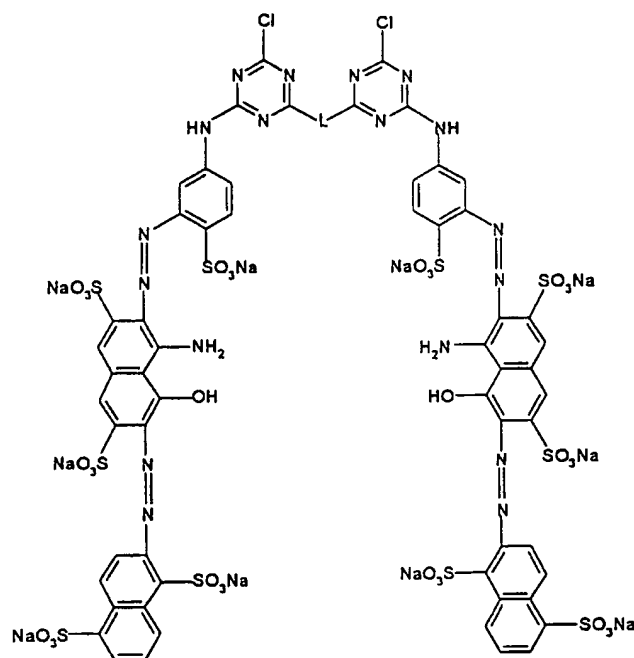
(D) T = 2,4-dichloro-1,2,5-triazin-6-yl

Ac = acyl

15

An aqueous solution of sodium 2-aminonaphthalene-1,5-disulphonate (0.12 mole in 200 ml water) and sodium nitrite (60 ml 2N) was added to stirred ice (200g) containing concentrated hydrochloric acid (30 ml) over 30 minutes maintaining the temperature below 5°C. Stirring was continued for a further 30 mins when excess nitrite was decomposed with 10% sulphamic acid solution. Intermediate (A) (ca 0.1mole) in water (800 ml) was treated with sufficient concentrated NaOH solution to ensure solution and cooled to below 5°C. This was added in a steady stream to the diazonium solution below 5°C whilst the pH gradually rose to 4 when coupling commenced. After 2 h at pH 4 below 5°C the pH was raised to 7 and the solution stirred overnight whilst warming to room temperature. The solution was filtered, the filtrate concentrated, and treated with methylated spirit to precipitate intermediate (B). This could be purified by redissolving in water and re-precipitating.

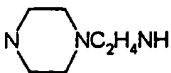
The protecting acetyl group was removed from intermediate (B) (0.1 mole) by hydrolysis with KOH (112g) in aqueous solution at 55°C for 2.5h. The alkaline solution was neutralised with hydrochloric acid and concentrated to give successive crops of deacetylated intermediate (C). This (0.0262 mole) was dissolved in water (600 ml) and cooled to below 5°C and then treated with excess cyanuric chloride (5.08g; 0.0275 mole) dissolved in acetone. The well-stirred mixture was maintained at pH 6-6.5 for 2h, after which insolubles were filtered off. The filtrate (containing 0.0131 mole dye (D)) was stirred with ethylenediamine (0.4g; 0.00655 mole) overnight at pH 10. The pH was then adjusted to 7 and the reaction mixture concentrated. Addition of methylated spirit precipitated the product (1; below) as a blue powder, which could be purified by dialysis. As can be seen from Table 1, this had $\lambda_{\max} = 616\text{nm}$, $\epsilon_{\max} = 86500$, 1/2-band width (HBW) = 117nm, and dyed cotton a greenish-navy shade with excellent all-round fastness properties.



Examples 2-30

By replacing the ethylenediamine of Example 1 by an alternative diamine or mercaptoalkylamine, LH_2 , analogues of (1) differing in the nature of the linking group, L, have also been prepared, as listed in Table 1.

Table 1

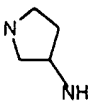

Example number	L in structure (1)	Shade on cotton	λ_{max} nm	ϵ_{max}	HBW nm
1	NHC_2H_4NH	greenish navy	616	86,500	117
2	$1,3-NHC_6H_4NH$	greenish navy	616	83,200	123
3		greenish navy	613	91,000	117
4	NHC_3H_6NH	greenish navy	617	91,100	116
5	$NHCH(Me)CH_2NH$	greenish navy	615	88,900	114
6	$NHC_2H_4N(Me)$	greenish navy	616	82,700	117
7	$NHC_3H_6N(Me)$	greenish navy	616	100,200	112
8	$NHCH_2CH(OH)CH_2NH$	greenish navy	616	91,500	114
9	$1,4-NHC_6H_4N(Me)$	greenish navy			

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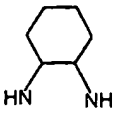
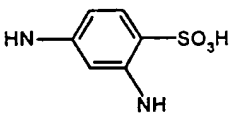
10	1, 4-NHC ₆ H ₄ CH ₂ NH	greenish navy	616	88,200	109
11		greenish navy	616	83,900	117
12	NHC ₂ H ₄ N (C ₂ H ₄ OH)	greenish navy	616	89,900	116
13	NHC (Me) ₂ CH ₂ NH	greenish navy			
14	NHC ₃ H ₅ N (C ₂ H ₄ OH)	greenish navy	616	89,600	113
15	NHC ₂ H ₄ S	greenish navy	615	90,100	123
16	1, 3-NHC ₆ H ₄ CH ₂ N (Me)	greenish navy			
17	NHC ₆ H ₁₂ NH	greenish navy			
18	NHC ₂ H ₄ N (C ₂ H ₅)	greenish navy			
19	NHC ₃ H ₆ N (Me) C ₃ H ₆ NH	greenish navy	622	108,400	110
20		greenish navy			

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21	1, 4-NHC ₆ H ₄ NH	greenish navy			
22	N(Me)C ₂ H ₄ N(Me)	greenish navy			
23	NHC ₂ H ₄ OC ₂ H ₄ NH	greenish navy			
24		greenish navy			
25	NHC ₃ H ₆ N(C ₃ H ₇)	greenish navy			
26	N(C ₂ H ₄ OH)C ₂ H ₄ N(C ₂ H ₄ OH)	greenish navy			
27	NHC ₂ H ₄ (OC ₂ H ₄) ₂ NH	greenish navy			
28		greenish navy			
29	HNCH(CO ₂ H)CH ₂ S	greenish navy			
30	N(i-Pr)CH(Me)CH ₂ NH	greenish navy			
31	(Et)NC ₂ H ₄ N(Me)	greenish navy	616	104,700	113
32	HNC ₂ H ₄ N(C ₃ H ₇)	greenish navy	616	99,900	113

Examples 33 - 62

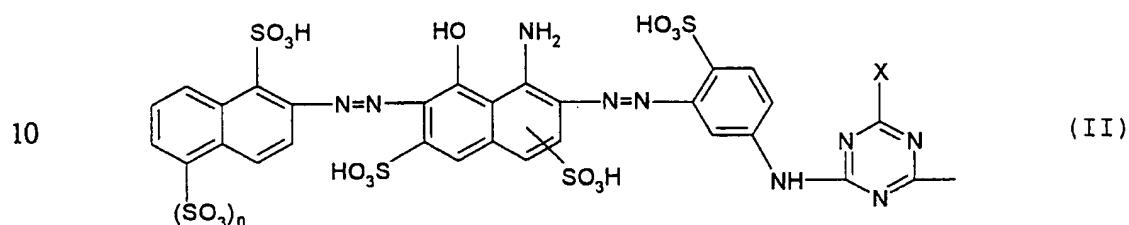
Each of the dyes prepared in Examples 1-32 was applied to cotton by exhaust dyeing at 90°C at a liquor :goods ratio of 10:1 and in the presence of salt and soda ash. In each case, the dye was found to have excellent build-up, extremely high fixation efficiency and good all round fastness properties.

CLAIMS:

1. A dye of the formula (I)



wherein each of D^1 and D^2 independently is a chromophore of the
5 formula (II)

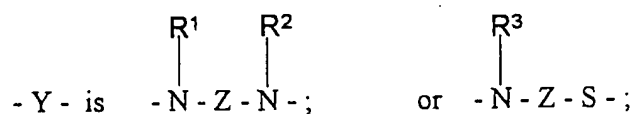


in which X is fluorine, chlorine or optionally substituted
15 pyridinium;

an SO_3H is present in the 5- or 6- position of the naphthalene
nucleus;

n is zero or 1; and

20



in which:

Z is a C_{5-12} aliphatic or aromatic cyclic hydrocarbon group,
optionally additionally containing at least one hetero atom
selected from N, O and S and optionally substituted by at least one
of C_{1-4} alkyl and SO_3H (or a salt thereof); or

at least two said cyclic hydrocarbon groups linked together;
or

a C_{1-15} alkylene or C_{2-15} alkenylene chain, which said chain

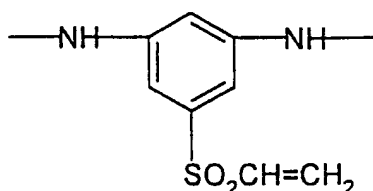
(a) optionally additionally contains, so as to be interrupted
5 or terminated by, at least one of (1) at least one hetero atom
selected from N, O and S and (2) at least one C_{5-12} aliphatic or

aromatic cyclic hydrocarbon group, which said cyclic hydrocarbon group (2) optionally additionally contains at least one hetero atom selected from N, O and S and is optionally substituted by at least one of C₁₋₄ alkyl and SO₃H (or a salt thereof); and

(b) is optionally substituted by C₁₋₄ alkyl, hydroxy-C₁₋₄ alkyl, amino-C₁₋₄ alkyl, hydroxyl, carboxyl or amino, which amino group or moiety is optionally substituted by one or two C₁₋₄ alkyl groups, or by a substituent group which, together with (i) one of R¹, R² and R³ (each defined below), (ii) the nitrogen atom to which R¹, R² or R³ is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group; and

each of R¹, R² and R³, independently, is a C₁₋₄ alkyl, hydroxy-C₁₋₄ alkyl or amino-C₁₋₄ alkyl group or each of R¹ and R², together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or (as defined above) one of R¹, R² and R³, together with (i) the nitrogen atom to which it is attached, (ii) the said substituent group on the chain Z and (iii) the said chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and

Y is other than



or a sulphonic acid salt of the said dye of the formula (I).

2. A dye according to claim 1, wherein Z is non-reactive.

3. A dye according to claim 1 or claim 2, wherein n is 1.

4. A dye according to any preceding claim, wherein the group SO₃H attached to the amino-bearing ring of the naphthalene nucleus is substituted in the 6-position thereof.

5. A dye according to any preceding claim, wherein Z is a C₁₋₁₀ alkylene chain optionally substituted by at least one group selected from C₁₋₄ alkyl, hydroxy and carboxyl groups.

6. A dye according to claim 5, wherein the C₁₋₁₀ alkylene chain is free from any hetero atom.

7. A dye according to claim 6, wherein the alkylene chain is a C₂₋₈ alkylene chain which is unsubstituted or substituted by at least one group selected from methyl, hydroxy and carboxyl.

8. A dye according to claim 7, wherein the alkylene chain is [CH₂]_x, wherein x is 2 or 3, which alkylene chain is unsubstituted or substituted by one or two methyl groups or hydroxy or carboxyl groups and each of R¹, R² and R³ independently is selected from hydrogen, C₁₋₄ alkyl and hydroxyethyl.

9. A dye according to claim 8, wherein Y is selected from NHC₂H₄NH; NHC₃H₆NH; NHCH(CH₃)CH₂NH; NHC₂H₄N(CH₃); NHC₃H₆N(CH₃); NHCH₂CH(OH)CH₂NH; NHC₂H₄N(C₂H₄OH); NHC(CH₃)₂CH₂NH; NHC₃H₆N(C₂H₄OH); NHC₂H₄S; NHC₂H₄N(C₂H₅); N(CH₃)C₂H₄N(CH₃); NHC₃H₆N(C₃H₇); N(C₂H₄OH)C₂H₄N(C₂H₄OH); HNCH(CO₂H)CH₂S and N[CH(CH₃)₂]CH(CH₃)CH₂NH.

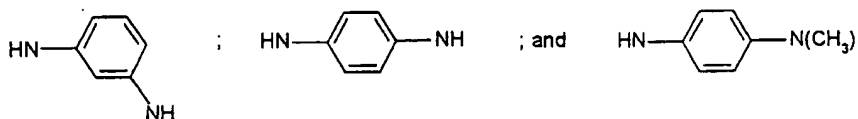
10. A dye according to claim 7, wherein Y is NHC₆H₁₂NH.

11. A dye according to claim 5, wherein the C₁₋₁₀ alkylene chain additionally contains at least one hetero atom selected from O and N.

12. A dye according to claim 11, wherein Y is selected from NHC₃H₆N(CH₃)C₃H₆NH, NCH₂H₄OC₂H₄NH and NHC₂H₄OC₂H₄OC₂H₄NH.

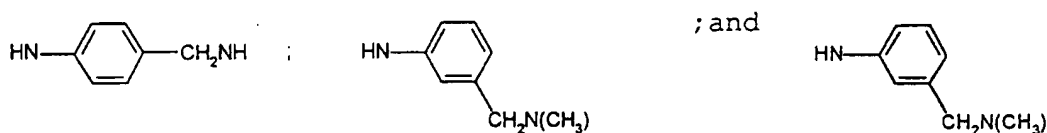
13. A dye according to any one of claims 1 to 4, wherein Z is a phenylene group, which phenylene group is unsubstituted or substituted by a sulphonic acid group and one or more methyl group(s).

14. A dye according to claim 13, wherein Y is selected from:



15. A dye according to claim 3, wherein the C₁₋₁₀ alkylene chain additionally contains at least one phenylene group.

16. A dye according to claim 15, wherein Y is selected from:

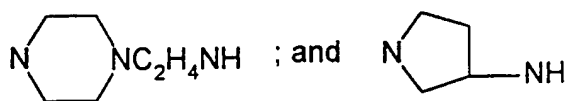


17. A dye according to any one of claims 1 to 4, wherein Z is a C₁₋₁₅ alkylene chain and is substituted by a substituent group which, together with (i) one of R¹, R² and R³, (ii) the nitrogen atom to which R¹, R² or R³ is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group.

18. A dye according to claim 17, wherein the C₁₋₁₅ alkylene chain is interrupted by a nitrogen atom, which nitrogen atom carries the substituent group.

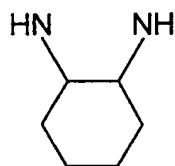
19. A dye according to claim 18, wherein Y is an imino-C₁₋₄ alkylpiperazinyll group.

20. A dye according to claim 17, wherein Y is selected from:



21. A dye according to any one of claims 1 to 4, wherein Z is an aliphatic cyclic hydrocarbon.

22. A dye according to claim 21, wherein Y is



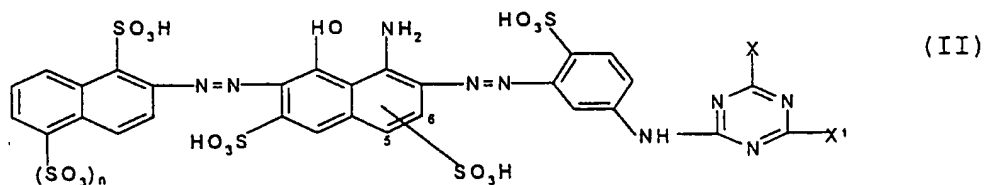
23. A dye according to any one of claims 1 to 4, wherein Z is a C₁₋₁₅ alkylene chain containing an aliphatic or aromatic cyclic hydrocarbon group, which group contains at least one hetero atom.

24. A dye according to claim 23, wherein Y is

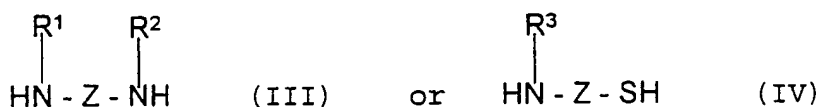


wherein n is 2 or 3.

25. A method of preparing a dye of the formula (I), given and defined in claim 1, which method comprises allowing at least one reactive disazo dye of the formula (II)

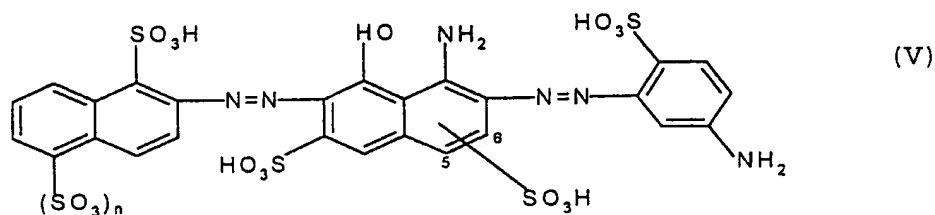


wherein X and n are as defined in claim 1 and X¹ is a fluorine, chlorine or optionally substituted pyridinium group, to react with a diamine or thioamine of the formula

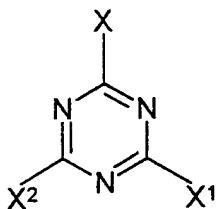


wherein each of R¹, R² and R³ and Z is as defined in claim 1, at a pH of from 7 to 10, in a proportional amount of two moles of reactive disazo dye (II) per mole of diamine or thioamine (III) or (IV).

26. A method according to claim 25, which includes the preliminary step of preparing the reactive disazo dye of the formula (II) by reacting a disazo dye of the formula (V)



wherein n is zero or 1, with a triazine of the formula



wherein each of X, X¹ and X² independently is chlorine, fluorine or optionally substituted pyridinium.

27. A process for the colouration of a substrate, which process comprises applying to the substrate, at a pH above 7, a dye according to any one of claims 1 to 24.

28. A process according to claim 27, wherein the dye is applied to the substrate by exhaust dyeing, padding or printing.

29. A process according to claim 28, wherein the dye is applied to the substrate by exhaust dyeing at a temperature of from 80 to 105°C.

30. A process according to claim 29, wherein the exhaust dyeing is carried out at a temperature of 85°C to 95°C.

INTERNATIONAL SEARCH REPORT

International Application No.

PLI/GB 99/02447

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B62/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 18224 A (CIBA GEIGY AG) 16 September 1993 (1993-09-16)	1-10
Y	page 48, paragraph 1 - paragraph 3; examples 99,100 page 20, paragraph 3 -page 21, line 2 ---	1-30
X	EP 0 458 743 A (CIBA GEIGY AG) 27 November 1991 (1991-11-27)	1-4, 15, 16, 25-28
Y	page 51, lines 1-10; page 14, lines 1-9; claims 1-8, 13, 14, 17-22 ---	1-30
Y	EP 0 625 551 A (CIBA GEIGY AG) 23 November 1994 (1994-11-23) cited in the application claims 1-7, 17, 18 ---	1-30
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

3 November 1999

Date of mailing of the international search report

18/11/1999

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/02447

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 818 513 A (ZENECA LTD) 14 January 1998 (1998-01-14) claims 1-5,7-9 ---	1-30
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